CHEMICAL: Metolachlor (108801)

FORMULATION: Technical

CITATION: Sumner, D. D.; Cassidy, J. E. (1974) The Uptake and Distribution of O-^{14}C-CGA-24705 from Soil in Greenhouse Grown Corn: CAAC-74015. Received Sept. 26, 1974 under 8G1553. (Unpublished report prepared by CIBA-GEIGY Corp. Greensboro, N. C.; CDL:94217-B).

TRADE SECRET CLAIM: Yes

REASON FOR REVIEW: Generic Standard for Metolachlor

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DATE OF REVIEW: January 23, 1978

TEST TYPE: Rotational Crop Uptake Study - Corn

OBJECTIVE:

1. To determine the uptake and distribution of CGA-24705 and its metabolites in greenhouse grown corn.

2. To characterize the plant metabolites based on ionic change and, solubility.

3. To further characterize dissipation and leaching of soil metabolites.

EXPERIMENTAL:

Silt loam soil (pH = 5.7; CEC = 8.4; organic matter = 3.6%, sand = 28.8%; silt = 66.4% and clay = 14.8%) was treated with ring labeled ^{14}C-CGA-24705 at a rate of 2 lbs per acre and spread as a 1/4 inch layer over Northrup King, Maycross - corn seeds planted one inch deep in the same type of soil in aluminum buckets. Greenhouse conditions were supplemented with artificial lights over a 12/12 hour day-night cycle. Corn samples were harvested by cutting at the soil surface at 4,8,12 and 16 week intervals. Four soil cores were taken in 3 inch segments to a depth of 9 inches at 0 time and at each harvest. All cores at same depth and time interval were composited. Homogenization of plants ( ) and blending of soil ( ) are referenced elsewhere as well as procedures for biphasic extraction with chloroform,

methanol and water to achieve organic soluble (non-polar) aqueous soluble (polar) and non-extractable fractions. Soils were extracted as a methanol water extract which in turn can be partitioned into organic and aqueous soluble fraction ( ). Additionally, refluxing with acetonitrile water was used for soil extractions ( ). Non-extractables were determined by a combustion procedure ( ).

The procedure of Knaah et al. ( ) was used to chromatograph methanol soluble plant metabolites. The column (anion-exchange) was 1.5 X 15 cm DEAE celllulose eluted with ammonium acetate buffer at pH 7.5 from over a concentration range of 0.01 to 0.1 m after adding the sample to the column.

Ionic components were characterized as neutral, basic, acidic or zwitterions after elution thru separate Dowex 1, Dowex 50 and mixed bed columns with water ( ).

Plant extracts were thin-layered on Analtech^{R} silica gel plates using chloroform: methanol: formic acid: water 75:15:4:2. Soil components in extracts were separated using nexane: chloroform: ethyl acetate 60:20:20.

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Degradation and Leaching in Soil

Table 1 shows the levels of activity at different soil depths immediately after treatment and at 4,8,12 and 16 week intervals. A rapid degradation appeared to occur in the early period (3.02 ppm in 0-3" layer at week 0 + 1 day) period going to 0.5 ppm in the same layer at 8 weeks. For the next 8 weeks little if any loss of total radioactivity occurred in the upper 3 inch layer. Although the data are somewhat variable, continued leaching into the lower layers is suggested.

Both total organic solubles (from MeOH/H_2O extraction and identified metolachlor (Using TLC) were significantly reduced in the period between the 4th and the 12th week while during this same period non-extractables increased from 60.5% to 78.8%. A substantial amount (10% of unknown extractables as determined by substracting ^{14}C metolachlor levels from total organic) was found in the 0-3" layer even at the 16 week sampling period. COncurrent balance studies using a CH_3CN extract suggested possibly even higher levels of organic unknown extractables.

Metabolites Residues by Corn Plants

The ^{14}C radioactive content of corn stalks decreased from 1.45 ppm equivalent to metolachlor at 4 weeks to 0.37 ppm at 12 weeks (silage stage). The authors ascribed an increase in residues in stalks at the 16 week harvest stage to .72 ppm as due to plant desiccation. Grain (wet basis?) at the time of harvest contained 0.05 ppm radioactivity expressed as metolachlor.

Partitioning studies indicated a high level of H_2O/MeOH soluble residue 80.7% of total at 4 weeks which continued on at least through the last accurate test period of 12 weeks (80.8% of total activity). Non-polar components as represented by chloroform extractables also stayed fairly steady, ranging from 5 to 6%. At both the 4 and the 12 week period the predominance of polar (H_2O/MeOH soluble) residue were found to be acidic in nature. Two dimensional thin-layer radiochromatograms of the methanol extract from 4 week old corn samples, using 75:14:4:2 $CHCl_3$, MeOH, HCOOH, H_2O showed the presence of at least 6 metabolites even though DEAE cellulose column chromatography suggested only one major component.

DISCUSSION:

1. This study used ring labeled metolachlor. Use of this material does not allow for conclusion with regard to the metabolic fate in soil or plants of the potentially important chloroacetaldehyde moiety which is a logically predicable product of N-dealkylation.

2. No model compounds were co-chromatographed on the TLC systems and it unclear whether CIBA-GEIGY even prepared such models (theorized) degradation products which might be expected to be products resulting from microbial degradation as mediated by soil, plant root exudates or soil microorganisms.

3. In general the protocol used is acceptable and the extraction and gractionation techniques were well conceived and applied. However, data on TLC is totally unsatisfactory. No explanation is given as to the appropriateness of the TLC system used for neutral, acidic and basic constituents. Conspicuously absent is the lack of attempt to identify extractable-organosoluble metabolites in soil. Such materials are readily amendable to extention of the techniques already reported.

4. Even though a preponderance of the plant metabolites in mature corn stalk are H_2O/MeOH soluble and acidic in nature, a total of .12 ppm (expressed as metolachlor) of organosoluble "nonpolar" material is present. No attempt was made to identify this material. Regardless of whether it is all metolachlor or not, the amount is too high to be disregarded.

5. Due to the large amounts of acidic-polar metabolites an attempt should be made to identify the major products and compare by co-chromatography with model compounds.

6. Decomposition of the 16 week sample of corn stalk, while influencing results, should have little influence is increasing organosoluble metabolites as contrasted to the more polar MeOH/$CHCl_3$ soluble. Therefore, the high value (16.7% $CHCl_3$ extractable) metabolites are potential cause of concern and would require close toxicological perusal.

TABLE I : PARTICLE CONCENTRATION[a] AND DISTRIBUTION OF METABOLITES[b] IN CLIMBORA SOIL[c] TREATED WITH 2 POUNDS PER ACRE OF ^{14}C

Interval (week)	0 + 1 Day		4			8			12			16		
Depth (inches)	0-3	3-6	0-3	3-6	6-9	0-3	3-6	6-9	0-3	3-6	6-9	0-3	3-6	6-9
Total ppm	3.02	0.03	1.92	0.73	0.43	0.50	0.20	0.25	0.69	0.43	0.30	0.65	0.24	0.14
Balance (MeOH Ext.)	Radioactive Distribution in Percent													
Organic			41.8			6.0						10.8		
H_2O/MeOH			5.7			6.0						3.1		
Non-extractable			50.5			86.0						78.5		
CGA-24705			39.4									3.6		
Unknown Extractable			10.1									10.3		
Balance (CH_3CN Ext.)														
Organic						18.0						19.8		
Polar						6.0						10.8		
Non-extractable						70.0						60.8		

(a) Expressed as ppm equivalent to [illegible].

(b) Expressed as % of total radioactivity.

(c) A silt loam soil.

TABLE 2. RADIOACTIVE METABOLITES PRESENT IN GREENHOUSE CORN TREATED PREEMERGENCE WITH 2-14C-2 POUNDS PER ACRE

Interval (week)[b]	4	8	12	15 Stalk[c]	15 Ear
Total ppm[a]	1.45	0.46	0.37	0.72	1.05
Balance[b]	Radioactive Distribution in Percent				
$CHCl_3$	4.2		5.4	15.7	
H_2O/MeOH	80.7		83.8	59.7	
Non-extracted	11.7		10.9	12.1	
Total Recovery	96.6		108.1	74.5	
Ionic Characterization of H_2O/MeOH Solubles[c]					
Neutrals	7.0		7.9	5.1	
Acids	73.1		53.6	37.7	
Bases	3.6		0.9	<0.1	
Zwitterions	5.2		21.4	16.7	

(a) Expressed as equivalent to ø-14 metabolite

(b) Refer to CDL:

(c) Refer to CDL:

(d) Decomposed during shipment.

CONCLUSIONS:

1. Metolachlor is steadily lost from the upper layers of field treated soil with the most probable cause being a leaching process. The data do not reveal whether the leaching was in the form of undegraded parent compound or degradation products.

2. Losses of metolachlor in the upper 3 inch layer of soil appear to decrease rapidly with time and by the 8th week show signs of leveling off.

3. Non extractable residues increase with time at the apparent expense of organic solubles.

4. Metolachlor per-se decreases with time both on an absolute and relative basis, but approximately 10% of the total remaining residues between the 4th and 16th week were found as unidentified organic extractables !

5. The nature of potentially important metabolic products in soil have not been elucidated!

6. Significant quantities of both organosoluble non polar and polar metabolites can be extracted from mature corn stalks and separated by portition fractionation.

7. The 0.05 ppm residue found in mature corn grain also have not been characterized.